RARE ELEMENTS AS ALLOYING ADDITIVES TO HEAT-RESISTANT STEEL

-USSR-

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FOREWORD

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- USSR -

According to the modern theory of heat resistance, the resistance
of metals and alloys to deformation and breakdown is basically deter-
mined by two factors: the strength of the interatomic bond and the
structure of the metal.

At high temperatures the importance of the strength of the inter-
atomic bond in crystals increases even more, since it determines the
temperature range of the existence of the strengthened metastable states
of the alloy, i.e., the softening temperature. The softening rate of
alloys is determined by the diffusion mobility of atoms.

The greatest hardening of alloys for high temperatures is achieved
by creating a fine heterogeneous structure. The majority of the heat-
resistant alloys obtain such a structure through the formation of dis-
perse crystals of the second phase. The increase in the heat-resistance
of these alloys is connected with the increased temperature of the
beginning of the formation of the second phase and the retardation of
the process of particle coagulation. The stronger the interatomic
bond, the slower the processes of coagulation of the precipitated phase
and the structural softening.

In many alloys functioning at high temperatures the strengthening
phase is represented by carbides.

In order to raise the softening temperature it is necessary that
the carbides deposited during disperse hardening possess strong inter-
atomic bonds. The strongest carbide-forming elements are the rare
metals: titanium, vanadium, zirconium, tungsten, molybdenum, niobium,
and others. However, the use of these elements to increase the resist-
ance of austenite and raise the heat resistance of steel is rendered
difficult by the fact that during crystallization they most frequently
form stable carbides found in the alloy in the form of a superfluous
phase and practically not interacting with the solid solution.

In complex alloy steels which are alloyed not only with a strong
carbide-forming rare element but also a metal less similar to carbon,
for example, manganese or chromium, less stable carbides are formed
which take part in the process of solution and precipitation in heat
treatment.

This complex alloying makes it possible to bring the titanium, vanadium, niobium, zirconium, and other elements with a great tendency toward carbide formation into a solid solution. The presence of these elements in a solid solution causes changes in the temperature and solution kinetics of the hardening phase and, consequently, changes in the temperature and kinetics of softening during aging.

By regulating the distribution of the alloying elements between the solid solution and the hardening phase it is possible to markedly increase the softening temperature of steel.

In this work we have taken a look at the effect of titanium, vanadium, and niobium on the structure and properties of heat-resistant chrome-nickel-manganese steel of the 5-15-8 type. The composition of the test alloys is given in Table I.

TABLE I

CHEMICAL COMPOSITION OF TEST STEEL

Chemical Composition in %

Brand	C	Mn	Si	Cr	Ni	S	P	Rare Elements
1	0.27	8.26	0.27	4.58	14.75	0.008	0.017	
T1	0.23	7.60	0.29	4.65	15.08	0.015	0.017	Ti-0.28
T2	0.27	7.63	0.30	4.87	15.08	0.012	0.015	Ti-0.73
T3	0.25	8.02	0.41	4.77	15.08	0.014	0.025	Ti-1.30
F1	0.24	8.00	0.29	4.96	15.08	0.011	0.023	V-0.29
F2	0.25	7.60	0.29	5.07	15.08	0.011	0.016	V-0.85
F3	0.26	7.90	0.29	5.24	15.00	0.010	0.016	V-1.41
N2	0.28	7.69	0.14	4.97	14.93	0.011	0.023	Nb-0.57
N3	0.27	7.89	0.23	5.04	15.71	0.011	0.024	Nb-1.23

Introduction into the test steel of 15% nickel and 8% manganese makes it possible to produce a stable austenite structure.

To the steel is added a total of 5% Cr, the minimal amount of chromium which assures the heat resistance of steel up to a temperature of 700° C. Alloying this steel with titanium, vanadium, and niobium, which have a lattice and atomic diameter quite distinct from the lattice and atomic diameter of gamma-iron, is to assure its hardening at high temperatures and to increase creep resistance through distortion of the crystalline lattice of the gamma solid solution and the associated increase in the shear stresses under deformation, as well as through complication of the composition by the precipitating phases of high thermal stability.

In the test brands of steel, we studied the internal transformations which take place in steel during heating at high temperature and aging processes at 500, 600, 700, and 800° C, we detected the optimal heat treatment systems, we made a phase and x-ray structural analysis, we studied the mechanical properties of steel at room temperature and at high temperatures, and we investigated the basic service properties, and creep and heat resistance.

All the brands of steel examined represent a gamma solid solution having great structural stability: the alpha phase was not found even after aging for 200 hours at a temperature of 800° C.

The second phase is the carbide phase, in steel representing a complex cubic carbide of chromium in which a part of the chromium atoms have been replaced by atoms of iron of the type $(Cr,Fe)_{23}C_6$; and in steel alloyed with titanium, vanadium, and niobium, having carbides of the type TiC, VC, and NbC.

In Fig. 1-7 there are curves showing changes in the hardness, specific resistance, and grain size of steel alloyed with titanium, vanadium, and niobium during heating at high temperature.

The increase in the specific electric resistance and the reduction in hardness at temperatures of 950-1050° C indicate a dissociation of the chromium carbide which can be detected by phase analysis in all brands of steel except N2. The increase in specific electric resistance at temperatures higher than 1100-1150° C in steel alloyed with titanium indicates the beginning of the dissociation of the TiC carbide, while at 1150-1200° C there begins the dissociation of the vanadium carbide and at 1250° the dissociation of niobium carbide.

The literature mentions higher temperatures for the dissocation of these carbides. Apparently the presence of chromium atoms in titanium, vanadium, and niobium carbides weakens the interatomic bond in their lattices and contributes to the transition of the carbides into solid solution at lower temperatures.

When tempered steel of the type 5-15-8 is reheated for a long period to a temperature of 500-800° C (quenching temperature of 1200° C), there are substantial structural modifications. At first we observe intensified etchability of grain boundaries, which is related to the precipitation of the secondary phase in these spots in the disperse state; then the second phase appears on the grain boundaries in the form of chains, and its separation inside the grain starts.

The change in hardness and specific electric resistance corresponds wholly to the changes in microstructure.

Titanium and, in particular, niobium stabilize the structure of 5-15-8 steel, reducing dispersion hardening and retarding the development of structural changes in repeated prolonged heating (see Fig. 11 and 12).

While in steel 1 the beginning of the separation of the second phase from the solid solution can be laid to short holding at a temperature of 600° C, in steel alloyed with titanium and niobium only holding for 200 hours at 600° C causes increased hardness.

TABLE 2

MECHANICAL PROPERTIES *

Brand of steel	Temperature C° — 20					Temperature C° — 400				
	σ_B kg/mm²	σ_S kg/mm²	s %	ψ %	a_k kg-m/cm²	σ_B kg/mm²	σ_S kg/mm²	δ %	ψ %	a_k kg·m/cm²
1	60.0	24.9	60.4	74.4	<36	58.2	18.1	53.6	62.6	<36
T1	59.0	24.7	41.4	52.4	22.5	56.4	20.7	39.6	44.5	23.4
T2	59.0	26.2	38.8	49.6	20.7	55.8	22.4	35.6	46.2	20.4
T3	58.9	30.6	34.4	63.4	18.7	—	—	—	—	22.6
F1	61.1	28.5	54.4	62.8	25.4	58.2	23.0	45.0	51.0	24.3
F2	91.0	69.3	19.6	46.6	11.2	76.6	58.4	19.6	44.5	10.6
F3	105.2	86.2	17.0	42.2	12.8	93.0	80.2	10.0	24.3	11.7
N2	52.2	23.9	38.2	52.3	19.8	47.6	19.6	34.4	39.9	20.4
N3	50.9	26.2	36.4	40.7	19.1	46.3	19.0	36.6	38.4	15.1

* Mechanical properties were determined with samples of heat-treated steel: hardening at a temperature of 1200-1300° C and aging for 20 hours at a temperature of 680-700° C.

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TABLE 2 (Cont'd)

MECHANICAL PROPERTIES *

Temperature C° Properties	500					600				
Brand of steel	σB kg/mm²	σS kg/mm²	δ %	ψ %	ak kg-m/cm²	σB kg/mm²	σS kg/mm²	δ %	ψ %	ak kg-m/cm²
1	52.0	16.3	50.8	63.0	<36	43.6	12.9	36.0	40.9	<36
T1	52.7	19.3	39.4	55.1	22.7	44.6	16.5	29.0	53.8	23.6
T2	45.1	20.6	33.6	45.2	22.5	42.0	16.8	28.0	51.6	23.2
T3	—	—	—	—	25.0	35.1	20.7	25.2	53.8	25.5
F1	52.2	18.8	50.9	61.5	20.2	45.6	17.2	33.6	41.5	23.4
F2	70.0	56.4	20.0	49.6	11.8	56.1	46.1	16.4	46.7	14.2
F3	87.1	73.6	12.0	36.8	12.9	69.3	61.6	13.6	45.1	13.1
N2	43.6	19.0	31.2	41.5	21.5	36.7	15.3	25.0	29.1	22.5
N3	43.3	18.5	28.6	37.6	17.6	39.5	17.0	28.8	42.5	19.9

*Mechanical properties were determined with samples of heat-treated steel: hardening at a temperature of 1200-1300° C and aging for 20 hours at a temperature of 680-700° C.

TABLE 2 (Cont'd)

MECHANICAL PROPERTIES*

Brand of steel	Temperature C° 700				
	σ_B kg/mm²	σ_S kg/mm²	δ %	ψ %	a_k kg-m/cm²
1	26.9	11.5	16.0	18.1	<37
T1	32.6	15.3	21.2	29.3	25.9
T2	35.5	17.0	22.0	30.1	28.8
T3	30.4	19.1	28.0	49.5	29.3
F1	33.6	15.9	17.8	20.8	36.6
F2	47.3	45.0	14.2	34.2	15.9
F3	65.0	61.2	8.0	19.0	13.5
N2	29.5	15.4	21.0	25.9	23.8
N3	28.3	16.3	26.6	36.0	20.2

*Mechanical properties were determined with samples of heat-treated steel: hardening at a temperature of 1200-1300° C and aging for 20 hours at a temperature of 680-700° C.

Vanadium, on the other hand, greatly increases the tendence of steel to age by increasing dispersion hardening, and also intensifies the occurrence of structural changes during aging by accelerating the separation of the carbide phase and its coagulation (see Fig. 13). Kinetic aging curves for F2 and F3 steels (0.15 and 1.41% vanadium) lie much higher than the curves for 1 and F1 steels. At an aging temperature of 800° C they show a drop in hardness as a consequence of the coagulation process, since the maximal separation of the finely dispersed carbides at this temperature takes place during the first hour of holding.

The effect of the elements under consideration on the mechanical properties of steel corresponds to their effect on the structural state. Vanadium greatly increases the strength characteristics of 5-15-8 steel: at room temperature the value for the maximum strength of F3 steel is three times greater than the maximum strength of steel 1, and the value of the maximum yield exceeds by 100% the yield limit of steel 1. Titanium and niobium have a slight effect on the strength of 5-15-8 steel, but by stabilizing the structure they lend stability to the mechanical properties at high temperatures (see Table 2). Titanium, vanadium, and niobium reduce the plastic properties of 5-15-8 steel at room and higher temperatures, but at temperature above $600-650^\circ$ C the plastic properties of steel alloyed with these elements exceeds the plasticity of steel 1 to the degree to which the amount of each of these elements is greater.

Particularly effective is the influence of these elements on the creep of 5-15-18 steel, which at a temperature of 600° C and a load of 11 kg/mm^2 has a creep rate of 2.4×10^{-4} 0/0 per hour. An increase in load to 12.5 kg/mm^2 or of temperature to 650° C causes a breakdown of the steel samples after several hours of testing.

From the graphs in Fig. 14 we can see that titanium, vanadium, and niobium greatly reduce the creep rate, and this particularly sharply when added to the steel in a small quantity when hardening takes place through the formation of a secondary phase — more stable than in the case of chromium carbide — in the finely dispersed state.

Mention should be made of the increase in the creep of F3 steel as compared with F1 and F2 steels at a temperature of 600° C and a stress of 12.5 kg/mm^2. Also, in steel containing niobium an increase in the amount of niobium leads to a certain increase in creep at a temperature of 600° C.

A consideration of the curves in Fig. 14 leads us to assume that for a specific testing pattern there is an optimal amount of the hardening elements at which steel shows the best resistance to creep.

The studies showed that titanium increases somewhat the heat resistance of 5-15-8 steel, whereas vanadium and niobium have no substantial effect on it.

On the basis of the work done we may draw the following conclusions:

1. It is practical to alloy heat-resistant steel of the austenite class with rare metals which have a great tendency toward the formation of carbides, in order to harden the metal and increase its mechanical and service properties.

2. Titanium, vanadium, and niobium substantially increase the mechanical properties at high temperatures and the creep resistance of heat-resistant 5-15-8 steel.

3. In alloying 5-15-8 steel there are optimal amounts of the alloying elements which give the best combinations of properties to the steel: titanium, approximately 0.70%; vanadium, not more than 0.80%; and niobium, approximately 0.60%.

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— Machinery Institute of the
Latvian Academy of Sciences

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Fig. 1. Hardness of steels 1, T1, T2, and T3 after
hardening at different temperatures.
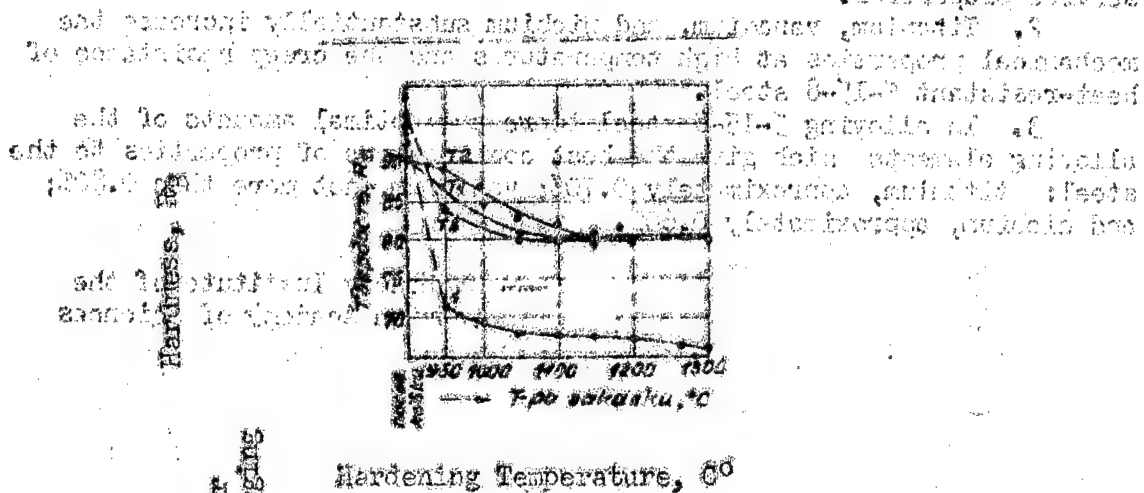
Hardening Temperature, C°
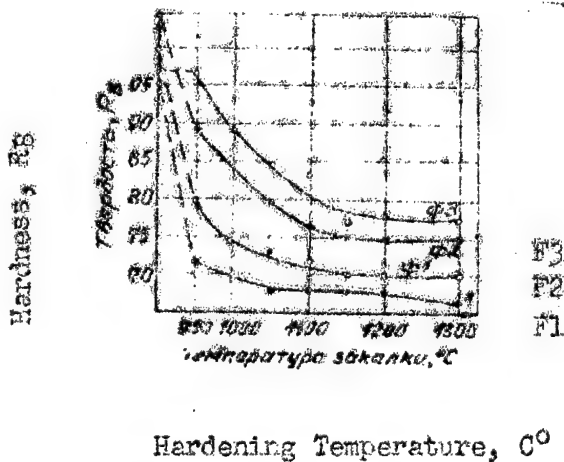
Fig. 2. Hardness of steels 1, F1, F2, and F3 after
hardening at different temperatures.
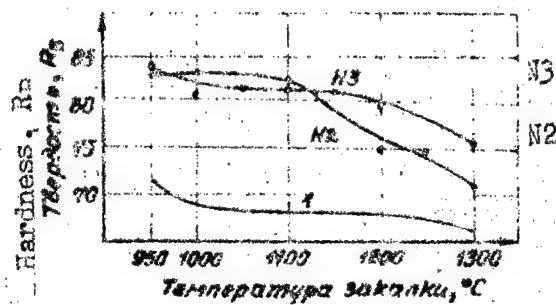
Hardness, Rn

Hardening Temperature, C°

Fig. 3. Hardness of steels N2 and N3 after hardening at different temperatures.

Specific electric resistance, M Ω/cm
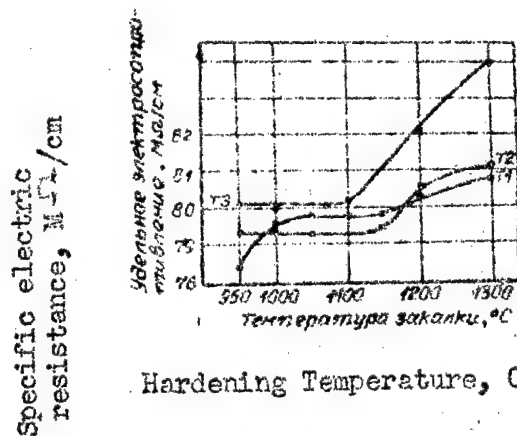
Hardening Temperature, C°

Fig. 4. Electric resistance of steels 1, T1, T2, and T3 after hardening at different temperatures.

Specific Electric
resistance, m–--/cm

F3
F2
F1

Hardening Temperature, C°
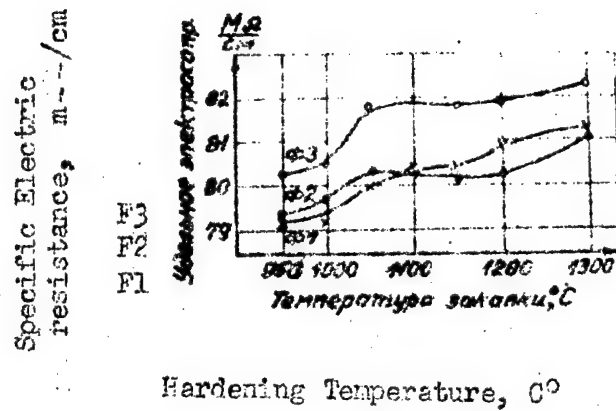
Fig. 5.   Electric resistance of steels F1, F2, and F3
after hardening at different temperatures.

Specific Electric
resistance, m–ω/cm

N2
N3

Hardening Temperature, C°
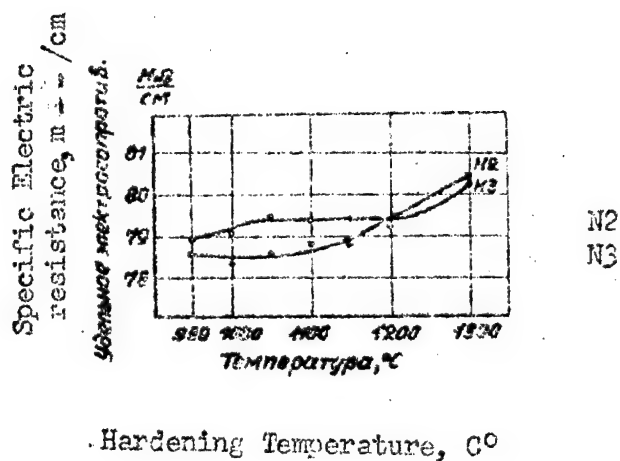
Fig. 6.   Electric resistance of steels N2 and N3
after hardening at different temperatures.

F1
F2
F3

N2

N3

Hardening Temperature, C°
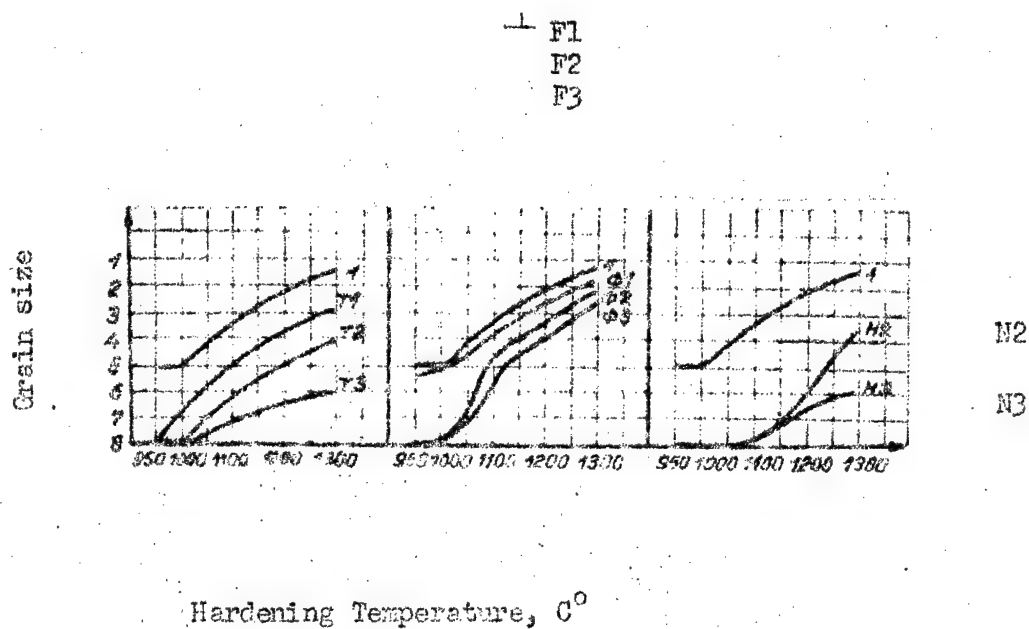
Figure 7. Effect of high-temperature heating on grain size in
the test steel. (Holding time during heating is
5 minutes)
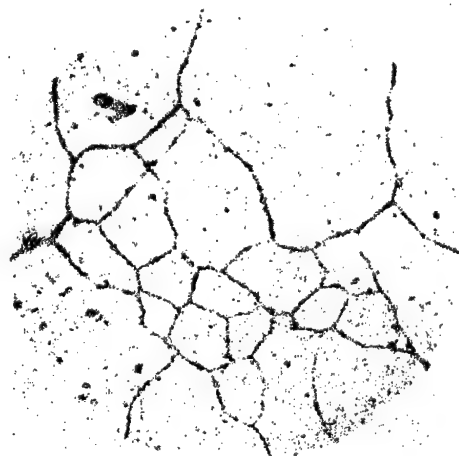
Figure 8. Microstructure of steel 1 after hardening at a
temperature of 1200° C. Magnification X300.

Fig. 9. Microstructure of steel 1 after hardening at a temperature of 1200° C and aging for 100 hours at 600° C. Magnification X300.
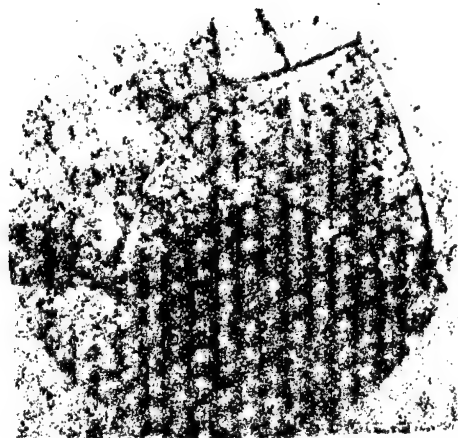

Fig. 10. Microstructure of steel 1 after hardening at a temperature of 1200° C and aging at 600° C for 200 hours. Magnification X300.
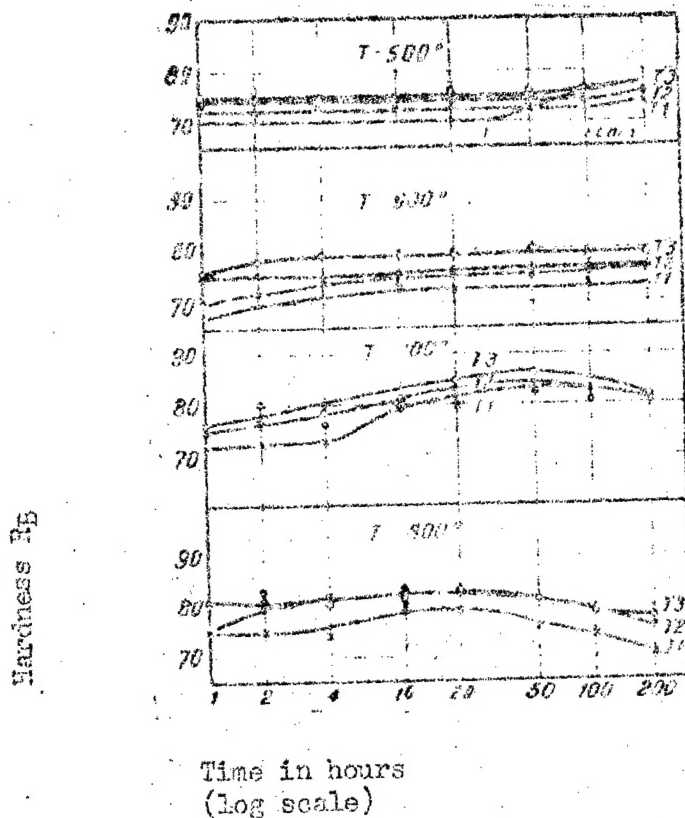
Time in hours
(log scale)

Fig. 11. Change in the hardness of steels 1, T1, T2, and T3 when aged at temperatures of 500-800° C.
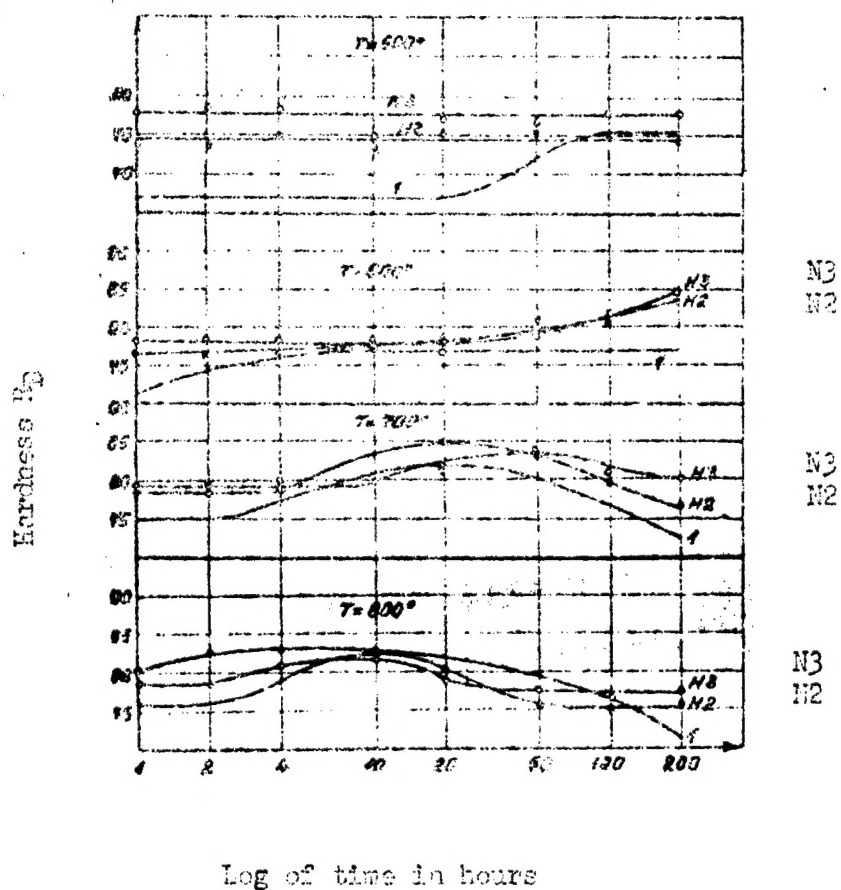
Fig. 12.   Change in the hardness of steels 1, N2, and
N3 when aged at temperatures of 500-800° C.

Fig. 13. Change in the hardness of steels 1, F1, F2, and F3 when aged at temperatures of 500-800° C.
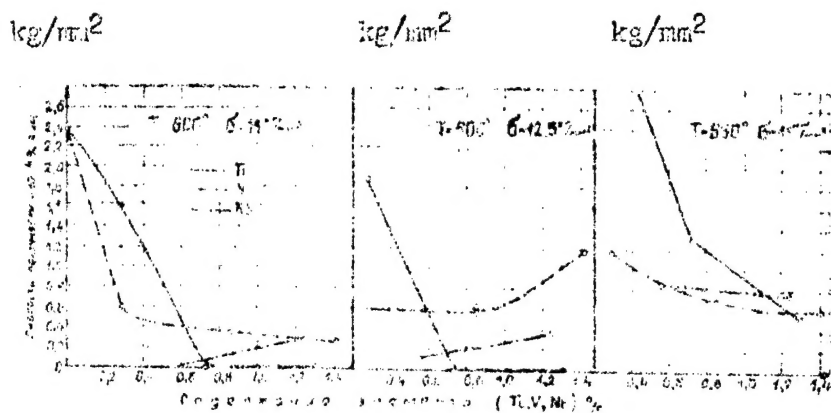
kg/mm²   kg/mm²   kg/mm²
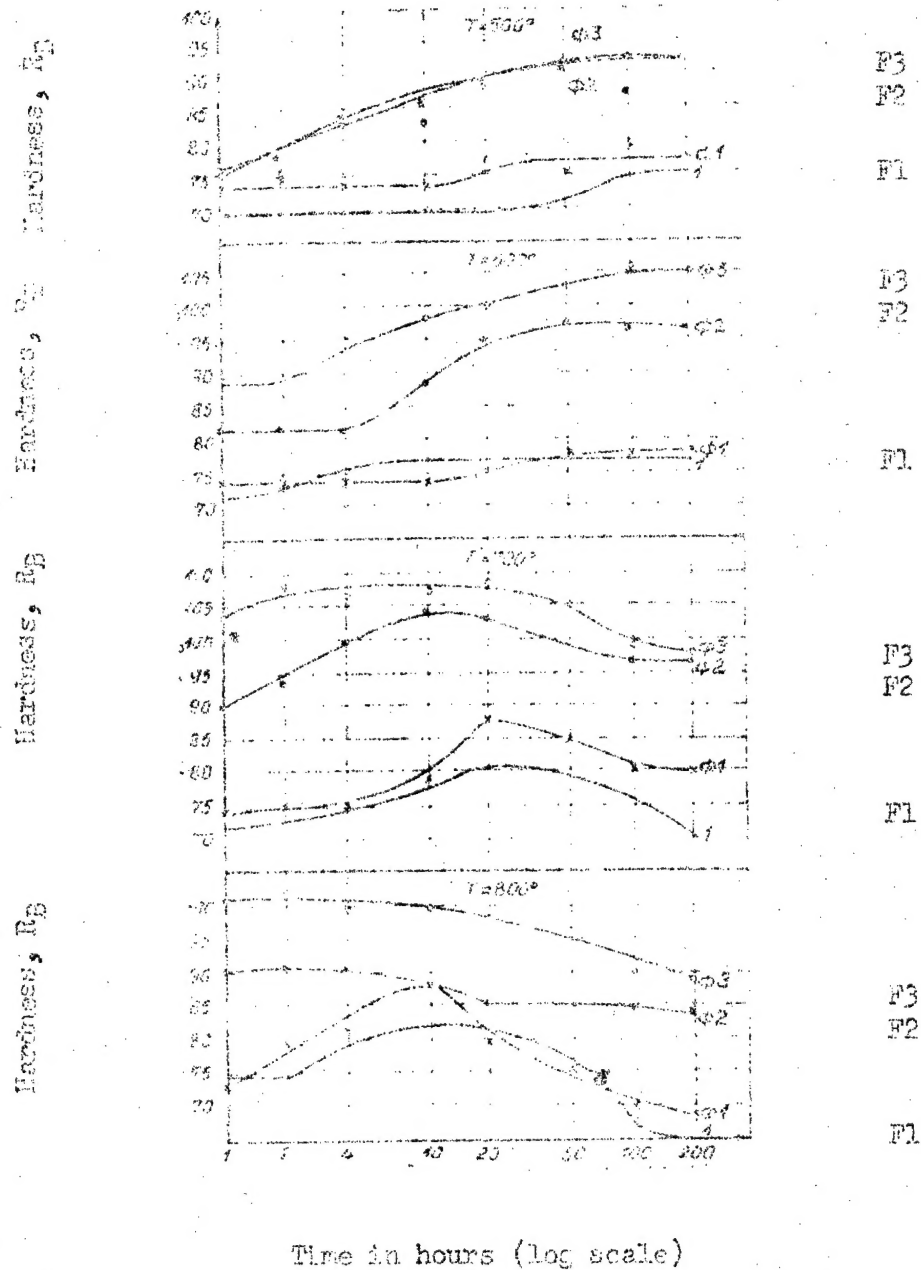
Amount of element (Ti, V, Nb) in %.

Fig. 14.   Effect of titanium, vanadium, and niobium on creep.